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RADIATION-THERMAL CRACKING OF CRUDE, OIL STOCKS AND HYDROCARBON GASES

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As shown in papers [I-8], the so-called radiation-thermal cracking (RTC) of hydrocarbons can be realized using both radiation and heat. This process can proceed with rates equal to those of pure thermal processes, but at temperatures by 150-200°C below than in thermal cracking or at similar temperatures, but with essentially higher yields. This is due to radiation which removes the activation barrier of the chain reaction initiation, the most energy-absorbing stage in thermal processes. On the assumption that irradiation makes changes only in the reaction initiation, it is easily seen that the higher yields in radiation-thermal cracking compared to those obtained thermally will depend on the dose rate of a radiation source and the rate ratios will decrease with increasing temperature. It should be noted that the higher the intensity of irradiation, i.e. the higher the rate of the reaction initiation by radiation, the higher will be the temperatures at which the radiation yields will exceed the thermal ones.

It should be pointed out that the initiation centres formed by ionizing irradiations are in large part "hot" and their distribution is not thermodynamically equilibrium.

The present paper reviews our investigations of radiation-thermal cracking at various experimental conditions of radiation on different hydrocarbon and oil stocks. The process was carried out in flow units using a) 800-kev fast electrons from a linear accelerator and b) mixed gamma and neutron irradiation from a nuclear reactor.

A study has been made of the effect of temperature, pressure and dose rate on RTC product yields.

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I. Fast electron irradiation in a linear accelerator

a) Radiation-thermal cracking with non-uniform temperature profile [6]

Radiation was carried out by about 800-kev electrons. The dose rate by acetylene dosimetry was 2×10^{16} ev/sec. per I ml of vapours under normal conditions. The flow sheet of the unit is outlined in Fig.I .

The conversion of the feed stock was determined by a difference between the fluid volume charged to the reactor and that condensed.

The gas volume formed was measured by a gas meter. The gaseous products were analysed for hydrogen and C_I-C_5 hydrocarbons by chromatography.

The liquid products and the feed stock were analysed in terms of specific gravity, refraction index, the unsaturate content by electrometric titration [10] and the fractional composition of light oil products. The total aromatic and unsaturate content of the liquid products was determined by the Kattwinkel method.

Various oil distillates were used as feed stock to the radiation-thermal cracking. Their characteristics are presented in Table I.

n-Heptane. Experiments on the radiation-thermal cracking of n-heptane, as with other feed stocks, were made at temperatures of 400° to 600°C. A relation has been found of the formation of gaseous products versus temperature for RTC and a radiation component (RC) has been derived for the above temperatures. The results obtained were compared to those of thermal cracking. Radiation-thermal cracking occurs at temperatures much lower than thermal cracking.

Of the most interest in this series of experiments is an increase in the unsaturate content of the C_2-C_4 fraction. It is seen from Fig.2 that the unsaturate percentage in radiation-thermal cracking rises very steeply with increasing temperature, exceeding 80%, while in thermal cracking it is only 50 to 55%.

I40°C E.P. straight-run gasoline and Krasnodar gas naphta. The gaseous product yield-temperature curves for radiation-thermal cracking of these gasolines (Fig.3) are similar in shape to those for n-heptane. In the case of the I40° E.P. gasoline the RTC gaseous

Table I. - Characteristics of feed stocks

Feed	n_d^{20}	d_4^{20}	Bromine no.	Sulphurizable, vol.%
I40°C E.P. straight-run gasoline	I.3886	0.6880	0.63	I3.6
Krasnodar gas naphta	I.3872	0.6750	I.7	I4.2
200°C E.P. straight-run gasoline	I.4I2I	0.7420	0.5	I4.8
200°C E.P. fraction from Tatar crude	I.4II5	0.7420	0.7	I6.4
250°-363°C middle gas oil	I.4758	0.86I5	3.0	3I.8

products are richer in the olefine content than in thermal cracking, which is supported by the data in Table II.

200°C E.P. straight-run gasoline from Tatar crude. In the radiation-thermal cracking of heavy gasolines the yields of gaseous products including olefines also increase with increased temperature, as outlined in Fig.4 .

Table II. - Yields of gaseous products in RTC and TC of I40°E.P. gasoline at different temperatures

	Temperature, °C	Yield of gaseous products, cm^3/g of feed								
		total	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10} (i+n)	C_4H_8
RTC	400	28.7	2.8	I0.I	2.8	3.0	0.7	2.I	2.5	0.9
	500	72.0	6.3	I9.8	7.4	I5.4	I.2	8.5	4.6	3.4
	600	206.0	I5	58	I6.9	43.2	3.9	26.2	I5.I	I3.I
TC	400	-	-	-	-	-	-	-	-	-
	500	I.6	0.3	0.5	0.06	0.2	0.02	0.04	0.22	-
	600	97	7.2	25.6	8.0	2I.6	I.6	I.2	7.2	4.8

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Yields of gaseous products and the unsaturate distribution at the temperatures that were maximum in our experiments are given in Table III.

Table III. - Yields of Gaseous Products in Thermal and Radiation-thermal Cracking at 550°C

Feed	Process	Yield, cm^3/g of feed							
		H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10} (i+n)	C_4H_8
200°E.P.straight-run gasoline	RTC	6.7	30.0	8.5	20.0	3.6	10.9	2.4	6.1
	TC	2.0	9.8	2.7	6.0	0.6	2.7	0.9	1.1
200°E.P. fraction from Tatar crude	RTC	9.5	30.6	13.0	36.6	1.2	13.0	2.4	9.5
	TC	2.2	8.7	3.9	9.1	0.2	3.2	1.5	1.9

<u>250°-363°C middle gas oil.</u> In the radiation-thermal cracking of middle gas oil an increase in yields of gaseous products is similar to that for the radiation-thermal cracking of light feed stocks, as can be seen from Fig.5 and Table IV.

Table IV. - Yields of Gaseous Products in Thermal and Radiation thermal Cracking of Middle Gas Oil at Different Temperatures

Process	Temperature, °C	Yield, cm^3/g of feed								
		total	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10} (i+n)	C_4H_8
RTC	450	22.6	5.7	3.9	1.0	8.5	1.0	3.6	0.6	1.0
	500	72.5	5.5	11.8	7.9	21.8	3.1	11.8	0.8	6.3
	550	100	3.0	19.9	13.5	33.6	4.0	16.6	-	9.9
TC	450	2.7	0.34	0.81	0.3	0.85	0.05	0.17	0.07	0.05
	500	7.4	0.5	2.0	1.0	2.7	0.2	0.8	-	0.2
	550	43	1.9	13.1	5.8	15.6	1.5	4.9	-	2.3

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b) Radiation-thermal cracking with uniform temperature profile [II]

The reactor used in the experiments with non-uniform temperature profile was so constructed that directly under the inlet port where electrons were introduced and where the radiation intensity was the highest the temperature was almost 200°C lower than that along the most of the reactor length taken as the temperature of an experiment. This certainly reduced the yields of RTC products and considerably distorted the actual temperature profile.

In order to obtain more single valued experimental data another series of experiments was made on the radiation-thermal cracking of the I40°C E.P. low-octane straight-run gasoline in an electron accelerator using a reactor of new design with uniform temperature profile provided with a lead bath.(Fig.6). The inlet port was inside the reactor, which prevents the cooling of beryllium foil and the distortion of the temperature profile under the inlet port.The large amount of molten lead as heat carrier provided high temperatures, intense heat exchange and uniform heating of feed vapours throughout the reaction zone.

The procedure was the same as in the previous experiments. The flow unit used was only a little different from that described earlier [9] .

The investigations with a reactor of new design were made wit the aim of estimating feed conversions and yields of gaseous products as a function of process temperature. As can be seen from Fig.7, the conversion in the experiments using the new reactor is almost twice as high as in the reactor with non-uniform temperature profile. Fig.8 shows that the yield of gaseous hydrocarbons including olefines much exceeds that in the experiments with a reactor of old design.

II. Radiation in a nuclear reactor

a) Procedure and feed characteristics

A special flow unit was developed for radiation-thermal cracking in the channel of a nuclear reactor [I2] . The flow sheet of the unit is presented in Fig.9 . The unit is designed for a horizontal channel of a nuclear reactor and can be used for flow processes

at temperatures of 400°to 600°C and pressures of I to 30 ata, the the pressure being determined by the vapours of the feed itself. The unit is provided with automatic control of temperature and pressure and with automatic sampling of gaseous products for chromatography. An electric heater assures temperature uniformity within the reaction zone.

Before operation the unit was placed into the reactor channel and checked for leakage by filling it with CO_2. The desired temperature conditions reached, the unit pressure was set up at a level determined by the feed vapours pumped with a constant rate. Fast neutrons and gamma-rays were used for radiation purpose; slow neutrons were absorbed by a boron carbide filter. The dose rate by ferrous-sulphate dosimetry was about $I0^{I5}$ ev/cm^{3}sec calculated for vapours at normal pressure and temperature. The experiment finished, the condensate was collected in a calibrated vessel and the system was blown with CO_2.

Thermal cracking was carried out in the same unit under the same temperature and pressure conditions, but outside the reactor channel. The analysss of the feed stock and the reaction products were made by a procedure similar to the described above. A 200°C E.P. fraction from Karadag condensate was used as feed stock to radiation thermal cracking. Table V presents the characteristics of the feed stock had been irradiated in sealed quartz ampoules for two hours in a neutron flux of about $4.I0^{I2}$ n/cm^{3}sec. The ampoules were unsealed nine days after the irradiation. The induced activity of the gasoline did not exceed the background.

Table V. - Characteristics of the 200°C E.P. Fraction of Karadag condensate

n_d^{20}	I.4I39
d_4^{20}	0.7435
Molecular weight	94.5
Iodine number	0.258
Sulphur, %	0.0I25
Group analysis, wt.%	
Aromatics	II.27
Naphthenes	29.56
Paraffins	59.I7

Temperature-yield curves for gaseous products of thermal and radiation-thermal cracking at atmospheric pressure, as shown in Fig.IO, are similar in shape to those btained in an electron accelerator [6,II] using a Co-source of radiation [I3] . Table VI shows the distribution of gaseous products of radiation-thermal cracking by the mixed gamma-neutron radiation.

Table VI. - Gaseous product distribution for radiation-thermal cracking at different temperatures

Temperature, °C	Distribution of gaseous products, %								
	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	C_5H_{12}
480	II.2	42.I	I3.4	25.2	2.8	-	5.3	-	-
530	7.4	43.5	IO.6	20.2	I.6	I2.2	2.2	0.9	I.3
570	6.6	54.7	6.5	I9.4	0.7	8.6	4.3	0.6	I.2

The comparison of the data given in Tables II and VI shows that the neutron irradiation contribution does not affect the gaseous product distribution. Table VI shows that the unsaturate content of the gaseous mixture decreases with increasing temperature; however, the absolute yield of unsaturated hydrocarbons increases, as can be seen from Table VII.

Table VII. - Gaseous product yields in radiation-thermal cracking at different temperatures

Temperature, °C	Yield, cm^3/g	
	C_2H_4	C_3H_6
480	5.6	-
530	36.4	2I.8
570	93.0	4I.4

It can be seen from the comparison of the RTC results with those of pyrolysis using the same feed stock (Table VIII) that the total yield of RTC gaseous products at 570°C is I.2 times as high as in

pyrolysis at 770° and the total unsaturate content is I.5 times as high.

Table VIII. - Yields of gaseous products in various processes

Process	Temperature, °C	Yield, wt.% of feed		
		total	ethylene	propylene
TC	570	II.0	2.0	I.8
RTC	570	68.0	I4.0	I2.5
Pyrolysis	770	52.2	I7.0	none

With increasing temperature there is a considerable change observed in the distribution of RTC liquid products. Table IX presents the characteristics of RTC liquid products at different temperatures.

Table IX. - Characteristics of RTC liquid products at different temperatures and a pressure of I atm

Properties	Temperature, °C		
	480	530	570
n_d^{20}	I.4I90	I.4309	I.4880
d_4^{20}	0.7458	0.7569	0.8459
Molecular weight	94.3	I00.I	I27.7
Iodine number	I5.9	I5.8	28.3
Unsaturates, %	5.9	6.2	I4.2

The kinetic treatment of the results obtained gives a value of 60±2 Kcal/mol for the total activation energy for pure thermal cracking, which is in agreement with the reported value. The activation energy of the assumed pure radiation process defined by the difference between the rates of radiation-thermal and thermal cracking is 23±3 Kcal/mol. The latter value is in good agreement with the values obtained using other radiation sources and other feed stocks [5,6, II,I3] . An assumed radiation-chemical yield of the RTC products

estimated by the difference between the RTC and TC rates in terms of molecules per I00 ev of energy absorbed is $I0^4$ to $I0^5$ molecules/I00 ev depending on temperature.

b) Pressure effect on radiation-thermal cracking

The total yield of gaseous products increases with increased pressure, linearly in the range of I to I0 atm. The yield of RTC products exceeds that of TC products, as shown in Fig.II . The unsaturate percentage of the gaseous products decreases with increasing pressure (Table X).

Table X. - Gaseous product distribution for thermal and radiation-thermal cracking at 480°C and different pressures

Pressure	Distribution, %									
	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	iC_4H_{10}	nC_4H_{10}	C_4H_8	C_5H_2
I atm										
RTC	II.2	42.I	I3.4	25.2	28.0	-	-	5.3	-	-
TC	-	-	-	-	-	-	-	-	-	-
I0 atm										
RTC	4.2	45.2	I3.8	9.5	7.2	I3.4	I.0	3.2	0.8	I.I
TC	5.5	54.2	II.4	9.3	3.7	I0.9	0.6	2.3	0.6	0.9
20 atm										
RTC	4.2	53.4	9.7	8.I	6.0	II.5	0.7	2.8	0.8	I.
TC	4.0	56.3	I3.8	5.8	6.2	9.0	0.8	2.2	0.6	0.8

This relationship was also observed by other authors [8,I3]. The yield of unsaturates reaches its peak at mean pressures of I to 3 atm and then decreases.

At a temperature of up to 530°C the ratio of RTC and TC yields is observed to decrease with increasing pressure (Fig.I2). While at a pressure of I atm W_{RTC}/W_{TC} is 4.5, it is only I.2 at a pressure of I0 atm.

There is a change in physico-chemical properties of the RTC liquid products with increasing pressure, as presented in Table XI.

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Table XI. - Characteristics of RTC and TC liquid products at 480°C and different pressures

Pressure	n_d^{20}	d_4^{20}	Mol.wt.	Iodine No	Unsaturates, %
I atm					
RTC	I.4I90	0.7458	94.3	I5.9	5.9
I0 atm					
TC	I.4220	0.7557	95.I	29.8	II.2
RTC	I.4335	0.7635	I03.6	25.4	I0.4
20 atm					
TC	I.3480	0.7684	I03.7	22.7	9.3
RTC	I.4I75	0.74I7	I05.8	23.I	9.I

III. Some future trends of radiation-thermal cracking

Our studies have shown that the yields of unsaturate gases amount to about 55% of feed and the unsaturate content of the RTC gases is about 70%; the liquid unsaturate content of the condensate is 45 wt.%. The over-all conversion per pass is approximately 75%. The radiation-chemical yield reaches $I0^3$ to $I0^5$ molecules per I00 ev depending on dose rate, temperature and pressure. Optimum yields and conversions in radiation-thermal cracking of various feed stocks can be obtained at a temperature range of 400 to 600°C and at pressures of I to 3 atm depending on dose rate.

However, such process conditions are far from being limiting. Yields can be increased first of all by increasing dose rate since over rather a wide range not studied yet at the upper end the radiation-chemical yield (G) is approximately proportional to $\sqrt{I}$, the slope of the corresponding curves depending on process temperature. It is evident that the number of initiating centres generated by radiation will so increase at some high dose rates that their recombination will prevent the further increase in the yields of desirable RTC products. Nevertheless, based on the data available, one can suggest with confidence that an increase in dose rate up to $6\text{-}8.I0^{I6}$ ev/cm^{3}sec should result in further increased yields and

some decrease in process temperature. Of essential importance for increasing yields and directed conversion are pure processing parameters, as shown by our direct experiments. Thus, the temperature profile corresponding to the kinetic and radiation features of the process resulted in higher yields without any other RTC parameters being changed. Of importance is also the dose field structure, the length and some other characteristics of communications, flow hydromechanics, the mixing rate and some others. Even partial and far from being optimum account of these factors has permitted us, without changing the utilities for both radiation and heating, to considerably increase the yields and the unsaturate percentage of the RTC products. It can be noted that heating is provided by the reactor off-heat.

The preliminary tentative estimates show that the RTC process is more effective in economics than pyrolysis in tube furnaces. In addition, the RTC permits the short-termed repayment of the expences on the nuclear reactor construction, in particular if the dracking hydrocarbon gases are used as a heat carrier, which are more suitable in terms of their heat physical properties than CO_2 and other gases.

It is necessary to point out that the RTC process proves to be economically effective not only at the stage of the cracking itself but also at the stage of gas separation that may be changed within a certain range at a sound choice of the process parameters. Another advantage of the RTC process is a sharp decrease in black- and gum formation compared to pyrolysis.

In addition, the RTC process consumes a very small portion (of the order of I to 2%) of the power chemical reactor output, which permits the use of the reactor both for other radiation-chemical processes using the charge stock obtained in the RTC process and as a source of electric and heat energy.

With this in mind, it seems to be sound practice to construct a combined group of refineries and petrochemical plants on the basis of a power chemical reactor as a source of radiation for radiation chemical processes and as a source of energy for petrochemical processes to be carried out using various products of radiation chemical cracking as feed stocks.

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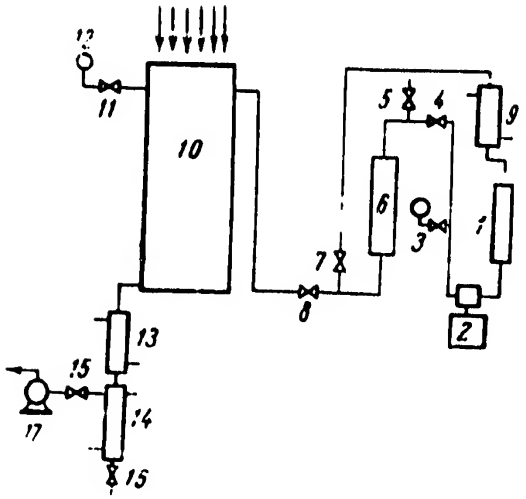

Fig. I Flow Diagram of RTC Unit.
I-measuring tank; 2- feed pump; 3, I2- pressure gauges; 4, 5, 7, 8, II, I5, I6- control valves; 6- vaporizer; I0- reactor; 9, I3- condensers; I4- gas separator; I7- gas meter.

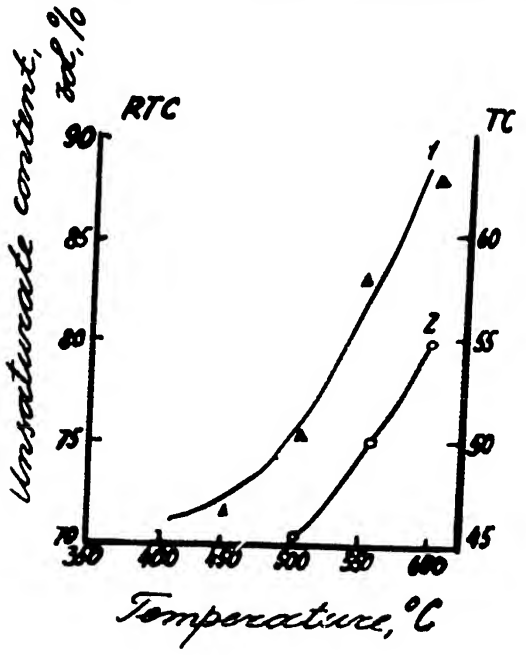

Fig. 2 Unsaturate Content of the C_2-C_4 Fraction vs. Temperature for RTC (I) and TC (2).

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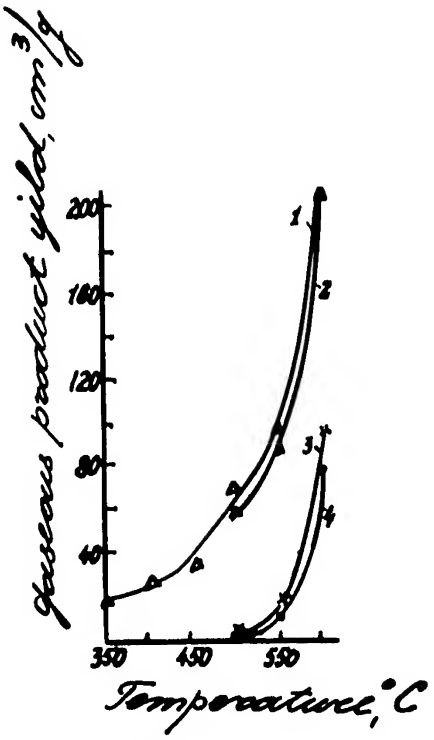

Fig. 3

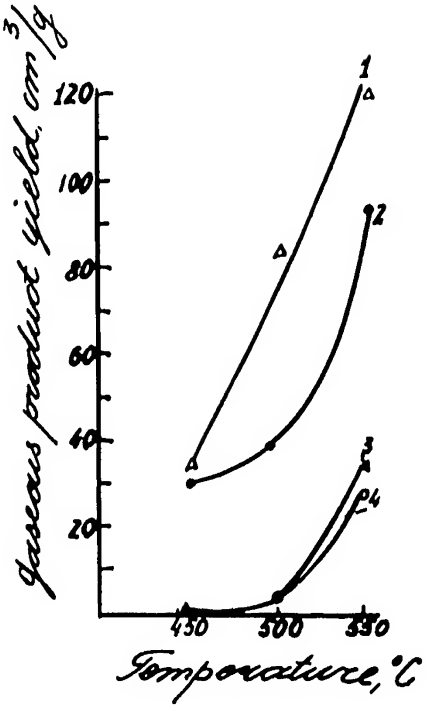

Fig. 4

Fig.3 Effect of Temperature on Gaseous Product Yields for RTC and TC.

I- RTC of I40°C E.P. gasoline, 2- RTC of Krasnodar gas naphta, 3- TC of I40°C E.P. gasoline, 4- TD of Krasnodar gas naphta.

Fig.4 Effect of Temperature on Gaseous Product Yields for RTC and TC of 200°C E.P. Straight-run Gasoline and 200°C E.P. Fraction from Tatar Crude.

I- RTC of the fraction, 2- RTC of the gasoline, 3- TC of the fraction, 4- TC of the gasoline.

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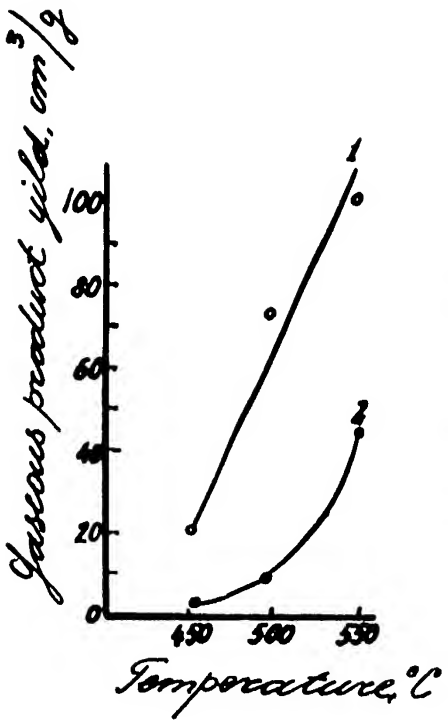

Fig. 5

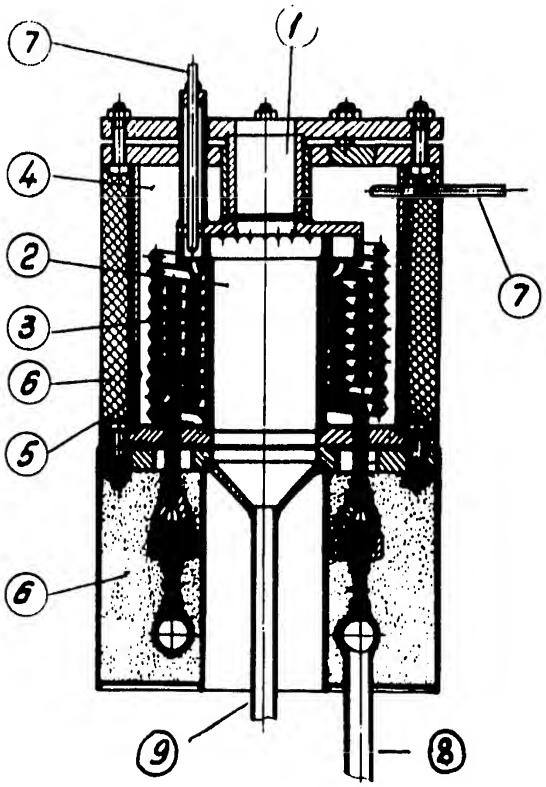

Fig. 6

Fig.5 Effect of Temperature on Gaseous Product Yields for RTC (I) and TC (2) of Middle Gas Oil.

Fig.6 Reactor with Uniform Temperature Profile

I- beryllium port, 2- reaction zone, 3- feed coils, 4- lead bath, 5-electric heater, 6- insulating layer, 7- thermocouples, 8- Collector for supplying vapours from a vaporizer to the reaction zone, 9- Product out.

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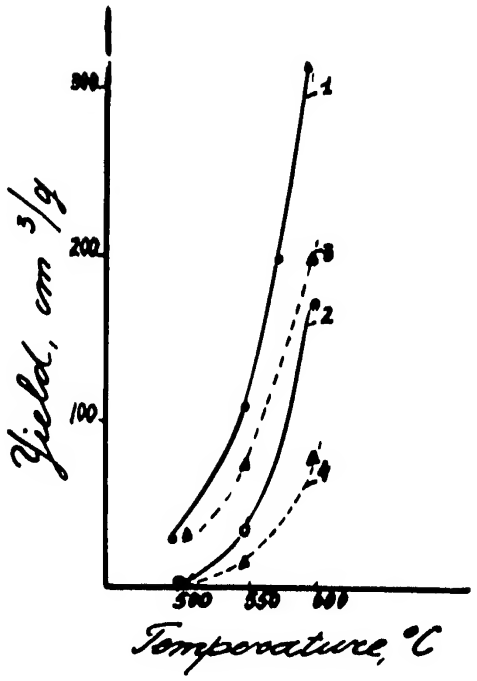

Fig. 7

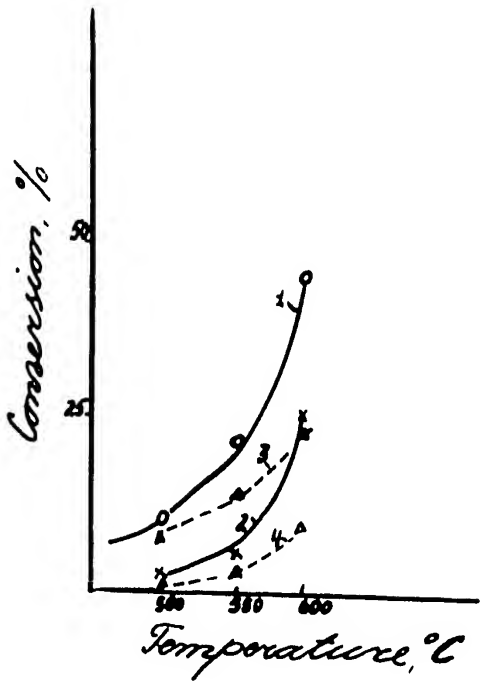

Fig. 8

Fig.7 Temperature-Conversion Relationship for Straight-run Gasoline with a I40°C End-Point.

I- RTC in a reactor with uniform temperature profile, 2- TC in the same reactor, 3- RTC in a reactor with non-uniform temperature profile, 4- TC in the same reactor.

Fig.8 Temperature Dependence of Gaseous Product Yields for RTC and TC of Straight-run Gasoline with a I40°C End-Point.

I- RTC in a reactor with uniform temperature Profile, 2- TC in the same reactor, 3- RTC in a reactor with non-uniform temperature profile, 4- TC in the same reactor.

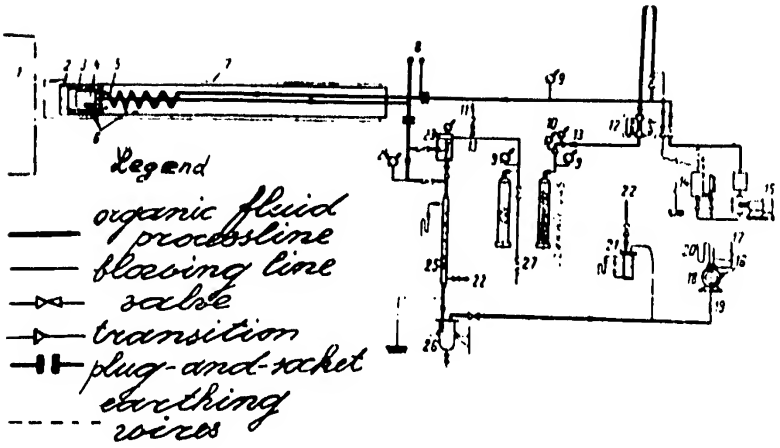

Fig.9 Flow Sheet of the Unit

I- nuclear core, 2- B_4C filter, 3- electric furnace, 4- reactor, 5- current-carrying tube-vaporizer, 6- thermocouples, 7- nuclear reactor channel, 8- current supply, 9, 24- precision pressure gauges (for the I to 60 atm range), I0- reducer (the range of 0-I50 to 0-60 atm), II- to atmosphere, I2- capillary flow meter (I00 atm), I3- capillary, I4- I.5-l feed tank, I5- liquid pump, I6- 0-50°C thermometer, I7- vent, I8- gas meter, I9- sample line to chromatograph, 20- U-shaped differential pressure gauge (600 mm of water column), 2I- hydraulic seal (600 mm of water column), 22- flowing water, 23- pressure control, 25- condenser, 26- gas separator, 27- blowing line.

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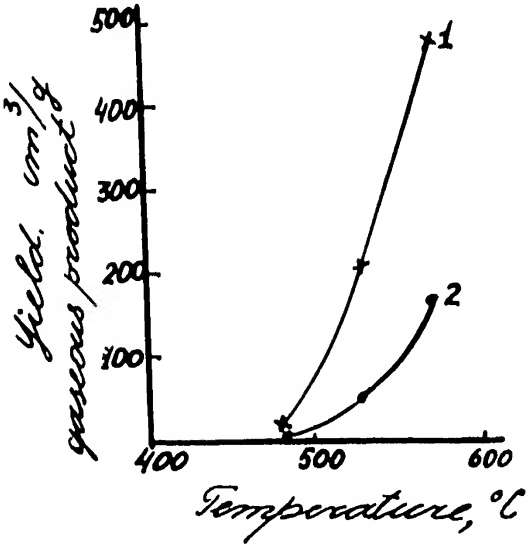

Fig.IO Temperature Dependence of Gaseous Product Yields for RTC and TC of the 200°C E.P. Gasoline Fraction at a pressure of Iatm.
I- RTC, 2- TC

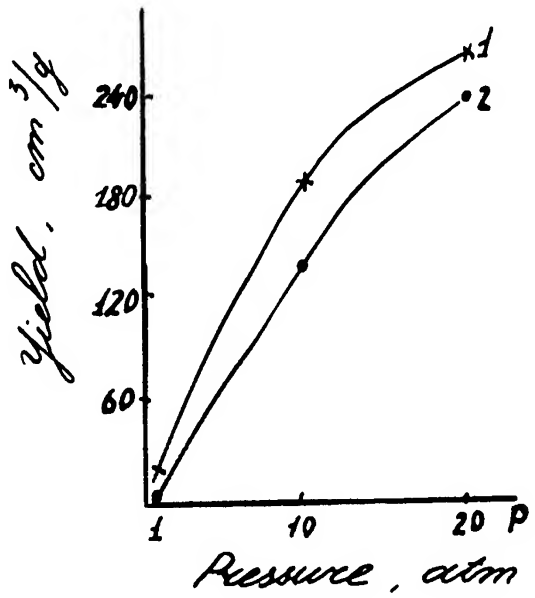

Fig.II Pressure Dependence of Gaseous Product Yields for RTC and TC of the 200°C E.P. Gasoline at a temperature of 480°C.
I- RTC, 2- TC